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ORIGINAL RESEARCH

The B–H–B bridging interaction in B-substituted oxazaborolidine–borane complexes: a theoretical study

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Abstract Ten oxazaborolidine–borane complexes, nine among them boron-substituted (B–R, R=CH_3, CF_3, and OCH_3), are carefully analysed using quantum-chemistry methods to determine their equilibrium geometries and the corresponding oxazaborolidine–borane interaction energies. It is observed that in all B-trifluoromethyl substituted oxazaborolidine–borane complexes and in one B-methyl substituted complex the B–H–B bond is formed and the interaction energies are 1.5–2.5 times as large as in other investigated complexes. We believe that the presented results may be helpful in experimental recognition of oxazaborolidine–borane complexes which may appear, inter alia, as reaction intermediates.

keywords B-substituted oxazaborolidine–borane complexes · B–H–B bond · Ab initio calculations · Density functional theory calculations · Intermolecular interaction energy

Introduction

Boron is known to form structures stabilized by strong delocalization of valence electrons [1]. A well-known example demonstrating strong unsaturation in boron compounds is borane, BH_3, which easily dimerizes into diborane, B_2H_6, forming electron-deficient three-center two-electron B–H–B bonds [2, 3]. Although very useful in many synthetic applications, gaseous diborane is, however, not convenient to handle and is thus commonly replaced in organic reactions by appropriate BH_3 complexes with tetrahydrofuran and dimethyl sulfide [4]. Oxazaborolidine-catalyzed asymmetric reduction of diverse functional groups with excellent enantiomeric excess is a remarkable example of successful application of borane–tetrahydrofuran and borane–dimethyl sulfide complexes in organic synthesis. During the last two decades an increasing interest has been observed in the asymmetric reduction of various types of organic compounds catalyzed by chiral oxazaborolidines, species recognized as catalysts in the Itsuno reaction [5] by Corey et al. [6–8], and thus often referred to as CBS catalysts. The CBS catalysts are very effective in enantioselective reduction of prochiral ketones [5], imines [9, 10], oxime ethers [11–14], and in formation of lactones [15]. High enantioselectivity and effectiveness of cationic oxazaborolidines have been reported for Diels–Alder reaction [16]. Moreover, biological activity of oxazaborolidines has also been investigated and some oxazaborolidines have been reported to show antibacterial activity against *Streptococcus mutans* [17]. The importance of

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oxazaborolidines in modern organic chemistry is indisputable and the large interest in this area resulted in several comprehensive reviews [18–21].

Large time savings in experimental procedure could be achieved if the oxazaborolidine–borane complexes used in the synthesis were purchased instead of prepared in situ from appropriate amino alcohols and borane sources, especially in the reactions employing stoichiometric amount of catalyst. However, development of stable oxazaborolidine–borane complexes has been reported to be a nontrivial task. Their short lifetimes and moisture sensitivity make them difficult to isolate, and thus structure of such complexes is rarely examined experimentally in more details [6, 22]. Contrary to oxazaborolidines, there are only two examples of oxazaborolidine–borane complexes in the Cambridge Structural Database [23], the first one isolated in 1992 by Corey et al. [24] and confirmed by Mathre et al. in 1993 [25], and the second reported in 2004 by Ortiz–Marciales et al. [26]. Structures of oxazaborolidine–borane complexes and their interaction energies are undoubtedly of primary importance for better understanding of the nature of intermolecular interactions in these systems, which determine their stability and affects mechanism of reactions involving these species.

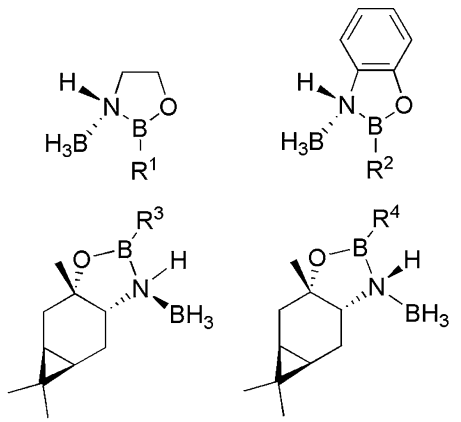
The reduction of ketones with borane in the presence of β-amino alcohols, catalyzed by formed in situ oxazaborolidines, has been extensively studied from both experimental and computational points of view. Extensive ab initio studies on model oxazaborolidines and their adducts with borane and symmetric carbonyl compounds were carried out in nineties by Nevalainen [27]. Linney et al. [28] investigated model oxazaborolidine–borane complex within the HF, MP2, and AM1 approximations. Moreover, theoretical studies on the mechanism of reduction of ketones were carried out using the semi-empirical MNDO [29] and AM1 [30, 31] methods as well as within the ab initio techniques and the density functional theory (DFT) [32–34]. Reduction of oxime ethers [35] and imines [36] has been the subject of detailed analyses using DFT. Despite extensive theoretical studies of oxazaborolidine–borane complexes it seems that only limited attention has been paid to the influence of the B-substituents in the oxazaborolidine ring on the geometry of the complex and its interaction energy.

In the present work the influence of B-substituent on geometrical parameters of ten carefully chosen oxazaborolidine–borane complexes **1**–**10** (see Fig. 1) and on their interaction energies is evaluated using computational chemistry methods. To our knowledge, this interesting subject has not been previously investigated. The geometries of the examined complexes are presently used by the authors in the studies on mechanism of reactions involving these species. Complexes **1**–**4** can be derived from 2-aminoethanol, **5**–**7** from 2-aminophenol, and **8**–**10** from recently reported 3-carene *cis*-β-amino alcohol [37, 38].

Computational details

Careful optimization of geometrical parameters of investigated systems is carried out using MP2 [39] (complexes **1**–**7**) and DFT [40, 41] B3LYP [42, 43] (complexes **1**–**10**) methods, and is followed by vibrational frequency calculations. The aug-cc-pVDZ basis set of Dunning and coworkers [44, 45] is used in geometry optimization and frequency calculations (aug-cc-pVXZ, X = *D*, *T*, *Q*, is abbreviated as aVXZ throughout the paper). Choice of the aVDZ set is based on the conclusions of Alagona et al. [34] that the 6-31G* geometrical parameters in system **1** are very close to those obtained using larger sets. Since the aVDZ basis set is larger and more diffuse than the 6-31G* basis we believe that no significant deterioration is introduced in values of geometrical parameters in investigated complexes. In particular, contrary to medium-sized Pople's basis set, the Dunning's correlation-consistent basis set are not found to suffer from spurious stationary points in the potential energy surfaces [46–48]. All optimized structures correspond to minima on the potential energy surfaces.

Borane molecule can approach oxazaborolidines derived from 3-carene either from the top face of the carene ring forming the *exo* complex (denoted with letter **a**) or from the bottom face forming the *endo* complex (denoted with letter **b**). Geometry optimization in both types of complexes **8**–**10** is performed. In B-methoxy-substituted oxazaborolidine–borane complexes (**4**, **7** and **10**), rotation of the methyl group around the O–B bond is also examined. Four starting points are used for each complex with the methyl group rotated by 90°. Two stable conformers are identified for each B-methoxy-substituted complex, the lower energy conformer with the methyl group pointing in the direction



1, R^1 = H; **2**, R^1 = CH_3; **3**, R^1 = CF_3;
4, R^1 = OCH_3; **5**, R^2 = CH_3; **6**, R^2 = CF_3;
7, R^2 = OCH_3; **8a**, R^3 = CH_3; **8b**, R^4 = CH_3;
9a, R^3 = CF_3; **9b**, R^4 = CF_3; **10a**, R^3 = OCH_3;
10b, R^4 = OCH_3

Fig. 1 Investigated oxazaborolidine–borane complexes **1**–**10**

of oxygen atom in the ring, and the higher energy one pointing in the direction of nitrogen atom. After test interaction energy calculation performed at the B3LYP/aVDZ level of theory, only the lower energy conformers are used in the regular interaction energy calculations.

The C^1–N–B^1–O dihedral angle (see Fig. 2 for atoms numbering) in the complexes is compared with the corresponding C^1–N–B^1–O dihedral in isolated oxazaborolidines whose geometrical parameters are optimized within the same approximation (B3LYP/aVDZ and MP2/aVDZ). For consistency with the study of complexes, optimization of the isolated methoxy-substituted oxazaborolidine geometries is carried out only for the conformers with the methyl group pointing in the direction of oxygen in the ring.

Optimized geometries are employed in calculation of the counterpoise corrected oxazaborolidine–borane interaction energies ΔE_{AB}. Interaction energies are evaluated neglecting the effect of geometry relaxation,

$$\Delta E_{AB} = E_{AB}^{\mathcal{AB}}(AB_{eq}) - E_{A}^{\mathcal{AB}}(AB_{eq}) - E_{B}^{\mathcal{AB}}(AB_{eq}). \quad (1)$$

Symbols E_{AB}^{AB} (AB) and E_{Z}^{AB} (AB) (Z = A, B) denote the energy of complex AB and of subsystem Z, respectively, calculated at equilibrium geometry AB_{eq} of the complex using basis set $\mathcal{AB}$ of the complex. In the following, we report M05-2X [49] interaction energies calculated with the aVQZ (complexes **1**–**7**) and the aVTZ (complexes **8**–**10**) basis sets using the B3LYP geometries. The M05-2X functional is chosen after careful computational tests carried out for complexes **1** through **7** within the MP2, CCSD(T) [50] and DFT approximations. DFT functionals employed in test calculations are: B3LYP [42, 43], B3P86 [42, 51], B3PW91 [42, 52], M05 [53], M05-2X [49], M06 [54], and M06-2X [54]. Depending on the size of the investigated system and the cost of the method, different aVXZ sets are used, with X up to Q. Complete set of interaction energies calculated within different approximations is reported in the Supporting Information.

Interaction energy values are reported in kcal mol^{-1}. All calculations are carried out using the GAUSSIAN 03 [55] and GAUSSIAN 09 [56] packages.

Results and discussion

Optimized structures of complexes **1** through **10** are presented in Figs. 3, 4, and 5. We start the discussion with noticing that geometries of investigated complexes can be divided into two groups, complexes with and complexes without a B–H–B bond. Formation of the B–H–B bond in system **1** has been previously reported by Linney et al. [28] and by Alagona et al. [34]. In the present paper we use the latter authors terminology referring to the structures without and the structures with B–H–B bridge as the *open* and the *closed* structures, respectively [34].

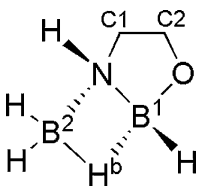


Fig. 2 Numbering of boron, carbon, and bridge hydrogen atoms in oxazaborolidine–borane complexes

The B–H–B bond is observed in all investigated B-trifluoromethyl substituted complexes and probably arises from the fact that the electron withdrawing CF_3 group decreases the electron density on B^1 atom. To compensate the resulting electron shortage B^1 forms the B–H–B bonding. In complexes containing the electron-donating methoxy or methyl group the B–H–B bond is not present, with the only exception being complex **5**, in which the B–H–B is formed but is somewhat weaker than the ones in B-trifluoromethyl substituted complexes. Formation of the B–H–B bond in complex **5** is probably caused by the electron-withdrawing character of the aromatic ring. The absence of B–H–B bond in complex **7** may result from compensation of the electron-withdrawing effect of the aromatic ring by the strong electron–donating character of methoxy substituent.

The B3LYP geometrical parameters of complexes **1**–**7** are in general in a very good agreement with their MP2 counterparts, see Table 1. The B3LYP functional somewhat underestimates the B^1–N, B^2–N, and B^1–O distances with respect to the MP2, predicts too small (absolute) values of the C^1–N–B^1–O dihedral angle for the complexes without the B–H–B bond, and too large (absolute) values for the complexes with the B–H–B bond. The overall agreement of the MP2 and B3LYP parameters is, however, encouraging. Values of the B^1–N, B^2–N, and B^1–O distances evaluated within both approximations are close to the experimental values reported for similar complexes [24–26], see Table 1. The agreement between the present MP2/aVDZ B^1–N and B^2–N distances in complex **1** (1.568 and 1.586 Å, respectively) and the available MP2/6-31G** data (1.558 and 1.574 Å, respectively) [28] is also quite satisfactory.

The B–H–B bond formed in investigated complexes is not symmetric. The distance between the hydrogen and the boron atom of the borane molecule is smaller than the one between the hydrogen and the boron in the oxazaborolidine ring, with the complex **6** being the only exception. The difference between the B^1–H^b and B^2–H^b distances depends on the system and is the largest in the case of complexes **1** and **5**. The B^1–H^b and B^2–H^b B3LYP distances in complex **1** (1.457 and 1.310 Å, respectively) are in perfect agreement with the B3LYP/6-31G* values reported by Alagona et al. [34] (1.457 and 1.30 Å, respectively). Small difference between the present MP2/

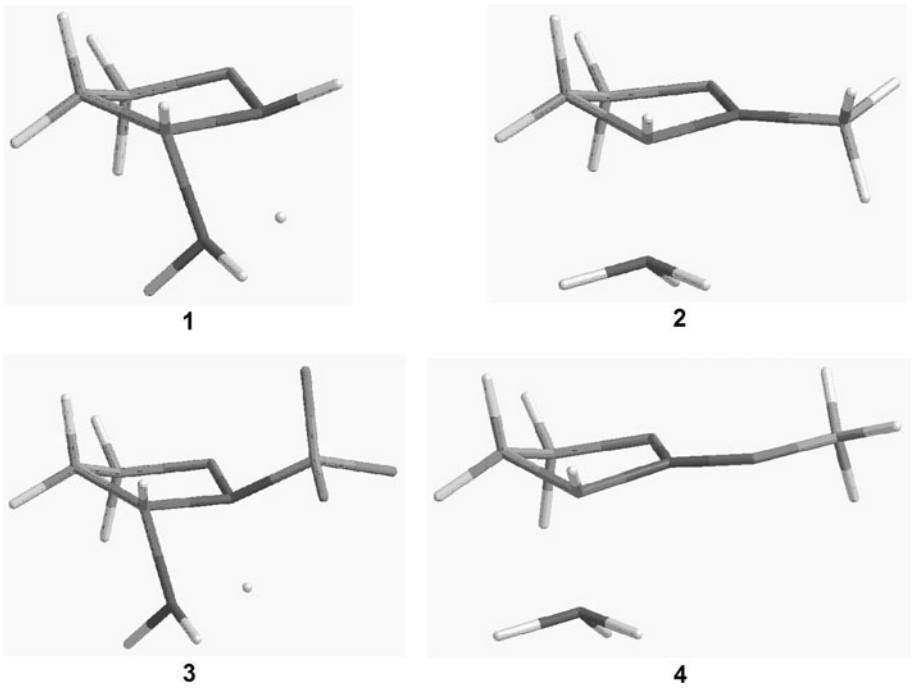


Fig. 3 MP2/aVDZ optimized geometries of systems **1**–**4**

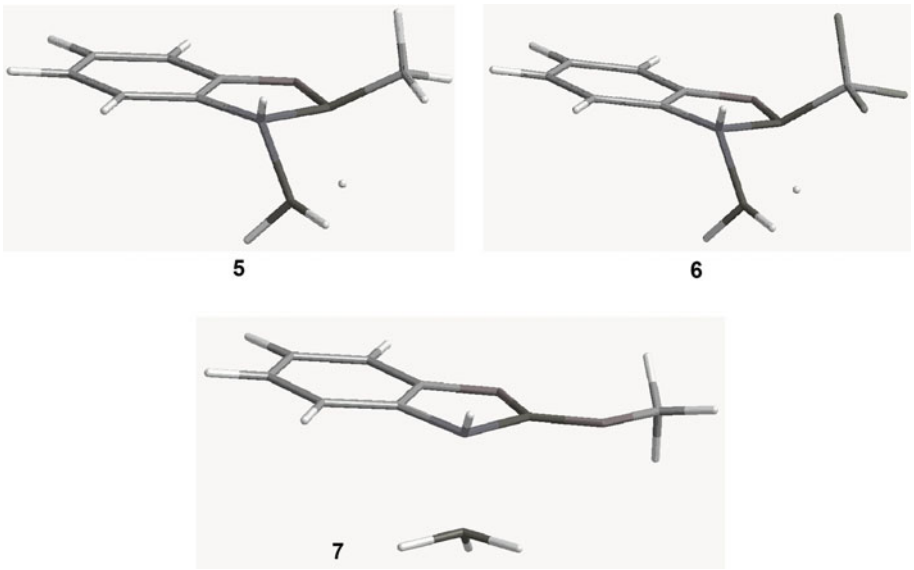


Fig. 4 MP2/aVDZ optimized geometries of systems **5**–**7**

aVDZ B^2–H^b distance in complex **1** (1.316 Å) and the corresponding MP2/6-31G** bond length reported by Linney et al. [28] (1.298 Å) is observed.

In the case of B-trifluoromethyl-substituted complexes, the two B–H distances are very close to each other making the B–H–B bond the most similar to the one observed in diborane. In the complexes in which the B–H–B bond is not observed the B–H distances in borane are in the order of 1.22 Å, while the presence of B–H–B bond in the complex forces the shortening of the B^2 bonds with the remaining two hydrogen atoms to approximately 1.20 Å—result in a good agreement with data reported by Linney et al.[28] for complex **1**. In all systems where the B–H–B bridging interaction is observed the B^1–N bond distance is in the order of 1.6 Å, in agreement with results earlier reported for complex **1** [28], and in the systems without the B–H–B bonding in the order of 1.7 Å. The latter value is in a good agreement with theoretical values by Quallich et al. [32].

Within the set of investigated systems, oxazaborolidine ring in isolated molecules is planar only in the case of oxazaborolidines derived from 2-aminophenol. Planarity is probably a result of aromaticity of C^1 and C^2 atoms. In all other cases, isolated oxazaborolidine ring is non–planar. The largest values of the C^1–N–B^1–O dihedral angle are observed in

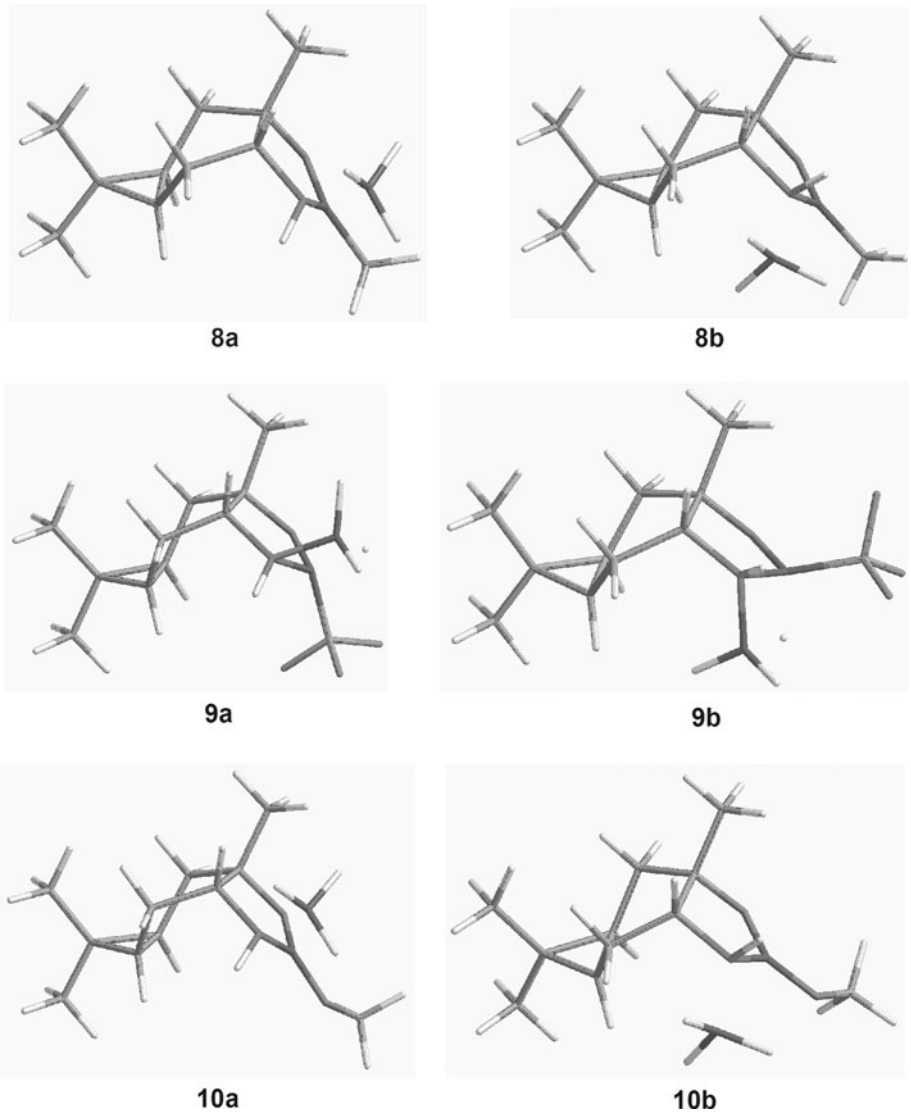


Fig. 5 B3LYP/aVDZ optimized geometries of systems **8**–**10**

oxazaborolidines derived from 2-aminoethanol. Smaller values of C^1–N–B^1–O dihedral in 3-carene oxazaborolidines are probably forced by the rigidity of the carene ring. Except oxazaborolidines derived from 2-aminophenol, isolated methoxy-substituted oxazaborolidines are characterized by larger value of the C^1–N–B^1–O dihedral angle than other oxazaborolidines derived from the same amino alcohol. Coordination of borane to oxazaborolidine causes a change in the value of C^1–N–B^1–O dihedral. Decrease (in absolute value) of C^1–N–B^1–O value with respect to isolated oxazaborolidine is observed for systems **1** and **3**, the latter only at the MP2 level of approximation. In all other cases value of the C^1–N–B^1–O dihedral increases (in absolute value). Formation of the B^2–N bond changes hybridization on the N atom from sp^2 to sp^3 and thus decreases planarity of the oxazaborolidine ring.

For systems **8** through **10** we observe that *exo* complexes are the lower energy structures. Although at the *exo* face two methyl groups are present, they are far from the nitrogen atom coordinating with borane and thus do not significantly influence the coordination process. Coordination from the bottom face is probably hindered by the steric interaction of borane with the carene ring, see Fig. 5. Within the B3LYP/aVDZ approximation energy of the **b** complex is about 4.5 kcal mol^{-1} higher than the energy of **a** for systems **8** and **9** and approximately 5.0 kcal mol^{-1} in the case of system **10**.

The M05-2X interaction energies in systems **1** through **10** evaluated using the B3LYP geometries are presented in Table 2. Additionally, the M05-2X//MP2 interaction energies and the estimated CCSD(T)//MP2 results in complexes **1**–**7** are reported (see caption of Table 2 for details). The M05-2X//MP2 values are in a very good agreement with the CCSD(T)//MP2 results. Differences between the M05-2X//B3LYP and M05-2X//MP2 values are in the order of 0.6–2.2 kcal mol^{-1}. It can be seen that

Table 1 The MP2/aVDZ and B3LYP/aVDZ geometrical parameters in oxazaborolidine–borane complexes

System	C^1–N–B^1–O[a]		B^1–N[b]		B^2–N[c]		B^1–O[d]	
	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP
1	−2.2 (−9.0)	−3.8 (−6.0)	1.568	1.555	1.586	1.580	1.425	1.409
2	−16.0 (−9.2)	−15.6 (−6.4)	1.512	1.507	1.685	1.681	1.372	1.361
3	−3.7 (−7.7)	−4.7 (−4.1)	1.559	1.553	1.580	1.572	1.417	1.404
4	−18.5 (−13.1)	−18.1 (−10.0)	1.505	1.501	1.682	1.679	1.379	1.367
5	−1.9 (0.0)	−3.2 (0.0)	1.583	1.576	1.601	1.593	1.461	1.448
6	−2.4 (0.0)	−3.2 (0.0)	1.572	1.567	1.589	1.579	1.445	1.434
7	−8.0 (0.0)	−7.7 (0.0)	1.506	1.503	1.731	1.727	1.400	1.389
8a	–	9.8 (2.6)	–	1.500	–	1.680	–	1.353
8b	–	9.1 (2.6)	–	1.514	–	1.669	–	1.352
9a	–	3.4 (2.5)	–	1.537	–	1.579	–	1.393
9b	–	−8.9 (2.5)	–	1.548	–	1.575	–	1.404
10a	–	12.6 (3.1)	–	1.494	–	1.680	–	1.360
10b	–	7.9 (3.1)	–	1.505	–	1.674	–	1.360

Angles in degrees, distances in Å

[a] Values in parentheses correspond to isolated oxazaborolidines

[b] Experimental B^1–N distances in similar complexes: 1.590(4) [26], 1.486 [24], 1.488 [25]

[c] Experimental B^2–N distances in similar complexes: 1.618(3) [26], 1.62 [24], 1.621[25]

[d] Experimental B^1–O distances in similar complexes: 1.436(3) [26], 1.335 [24], 1.348 [25]

Table 2 Oxazaborolidine–borane interaction energies in complexes **1–10**

System	Basis	M05-2X// B3LYP	M05-2X// MP2	CCSD(T)// MP2
1	aVQZ	−69.06	−71.27	*−71.17*[a]
2	aVQZ	−45.38	−44.77	*−44.81*[a]
3	aVQZ	−79.66	−81.36	*−80.04*[b]
4	aVQZ	−45.32	−44.44	*−44.55*[b]
5	aVTZ	−64.14	−65.05	*−63.70*[c]
6	aVTZ	−78.28	−78.58	*−75.66*[c]
7	aVTZ	−33.65	−32.18	*−32.47*[c]
8a	aVTZ	−45.51	–	–
8b	aVTZ	−47.74	–	–
9a	aVTZ	−73.97	–	–
9b	aVDZ[d]	−79.86	–	–
10a	aVTZ	−44.90	–	–
10b	aVTZ	−45.15	–	–

All values in kcal mol^{-1}. Symbol *A//B* denotes interaction energy calculated within approximation *A* using geometrical parameters optimized within method *B*

[a,b,c] Results estimated from MP2 results according to: $\Delta E_{CCSD(T)}(L) = \Delta E_{MP2}(L) + \Delta E_{CCSD(T)}(M) - \Delta E_{MP2}(M)$, with *L* and *M* denoting the large and the medium size basis sets, respectively [57–59]. [a] M = aVTZ and L = aVQZ; [b] M = aVDZ and L = aVQZ; [c] M = aVDZ and L = aVTZ

[d] The aVTZ results not available due to convergence problems

oxazaborolidine–borane interaction energies in *closed* structure complexes are approximately 1.5–2.5 times as large as in the *open* structure complexes. The increased interaction energy and thus higher stability of some of the examined oxazaborolidine–borane complexes give some hints where to look for possible stable complexes which would hopefully be easier to isolate. Without a detailed computational study it is not trivial to judge if increased stability of the oxazaborolidine–borane complexes may result in decreasing their reactivity or not. However, pentafluorophenyl-B-substituted oxazaborolidines, species relatively close in chemical character to the investigated trifluoromethyl-B-substituted oxazaborolidines, are successfully employed in organic synthesis proving to be efficient catalysts. Therefore, the trifluoromethyl-B-substituted oxazaborolidines discussed here also might turn out to be very efficient catalysts.

Conclusions

Detailed theoretical study of carefully chosen B-substituted oxazaborolidine–borane complexes was presented. In complexes **1** and **5** and in all B-trifluoromethyl substituted complexes formation of B–H–B bond is observed at both, MP2 and DFT/B3LYP levels of approximation. The oxazaborolidine ring in these *closed* structure complexes is

more planar than in *open* complexes due to the presence of rigid hydrogen bridge connecting the boron atoms. Oxazaborolidine–borane interaction energies in *closed* complexes are 1.5–2.5 times as large as in the *open* structure complexes. The largest interaction energy values are obtained in the case of B-trifluoromethyl substituted complexes. This probably arises from the fact that strong electron withdrawing CF_3 group substantially shifts the electron density from B^1 atom which in turn compensates the resulting shortage in electron density by forming the B–H–B bond.

Relatively strong interaction observed in B-trifluoromethyl substituted complexes suggests where to look for oxazaborolidine–borane complexes of higher stability. Although many factors have been neglected in our computational treatment (e.g., lack of solvent effects) it is possible that B–CF_3 substituted oxazaborolidine–borane complexes would be easier to isolate than other studied complexes.

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